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16. ABSTRACT

The persistence and disappearance (washoff or dryfall) of methoxychlor (2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane) from mature soybean (Glycine max (L.) Merrill) foliage was investigated in a small field plot study under natural rainfall conditions in 1977 and 1978. Residue analyses were conducted using whole plant samples. Methoxychlor washoff rate was 8± 4 % of the amount on plants (prior to rain) per centimeter of rainfall, regardless of time after application. Total seasonal washoff for 1978 accounted for 33.5 % of the applied pesticide; however, 30.5 % of the toral loss was removed by washoff on the second day after application. Dryfall or dislodgeable residue accounted for less than 1 % of the amount applied. The amount of dryfall was significantly greater in plots entered by workers than in those where entry was avoided. More than 19 % of the applied methoxychlor was lost as a result of through-fall to the ground during application to the plots. Statistical analyses indicated that within-sample variation for mechanical chopping of plant samples was significantly less at the 5 % level than for a hand chopping method. Results from this study will be useful in defining research objectives for the development of algorithms to describe the behavior of foliar-applied compounds. Such algorithms are necessary for estimating runoff losses of insecticides to water bodies.

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THE PERSISTENCE AND DISAPPEARANCE BY WASHOFF AND DRYFALL OF METHOXYCHLOR FROM SOYBEAN FOLIAGE--A PRELIMINARY STUDY

Key Words: Methoxychlor, dislodgeable residues, persistence, washoff, soybeans.

C.N. Smith, W.R. Payne, Jr., L.A. Mulkey, J.E. Benner, R.S. Parrish*, and M.C. Smith**

U.S. Environmental Protection Agency
Environmental Research Laboratory
Athens, Georgia 30613

*Computer Sciences Corporation
under U.S. EPA Contract
Environmental Research Laboratory
Athens, Georgia 30613

**Department of Biological and Agricultural Engineering
North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

The persistence and disappearance (washoff or dryfall) of methoxychlor [2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane] from mature soybean [Glycine max (L.) Merrill] foliage was investigated in a small field plot study under natural rainfall conditions in 1977 and 1978. Residue analyses were conducted using whole plant samples. Methoxychlor washoff rate was 8± 4% of the amount on plants (prior to rain) per centimeter of rainfall, regardless of time after application. Total seasonal

washoff for 1978 accounted for 33.5% of the applied pesticide; however, 30.5% of the total loss was removed by washoff on the second day after application. Dryfall or dislodgeable residue accounted for less than 1% of the amount applied. The amount of dryfall was significantly greater in plots entered by workers than in those where entry was avoided. More than 19% of the applied methoxychlor was lost as a result of through-fall to the ground during application to the plots. Statistical analyses indicated that within-sample variation for mechanical chopping of plant samples was significantly smaller at the 5% level than for a hand chopping method. Results from this study will be useful in defining research objectives for the development of algorithms to describe the behavior of foliar-applied compounds. Such algorithms are necessary for estimating runoff losses of insecticides to water bodies.

INTRODUCTION

The physical and chemical behavior of agricultural chemicals, especially pesticides, in the environment are of increasing concern as the use of these materials increases in response to demands for energy-efficient production of food and fiber. Although pesticides are widely used in farming and forestry, adequate data are lacking about the environmental behavior of those foliar-applied (or soil-applied) chemicals that can reach surface and ground water, posing potential exposure risks to humans.

Once an insecticide is applied and intercepted by plant foliage it may become adsorbed, absorbed, volatilized, degraded (chemical, photochemical, microbial) or be removed from the plant by wind and rain[1] as well as by animal disturbance. When the material is dislodged from the plant and comes in contact with the soil, it may still undergo changes through similar pathways as on plants, but it also has the potential to move away from the target zone by runoff[2]. Also, runoff losses are higher for foliar-applied organochlorine insecticides than for other pesticides because of the persistence of organochlorines and the large quantities that are applied[3]. Their toxicity is such that runoff losses can result in fish kills. It is generally known that pesticide runoff losses increase as application rates increase. In recognition of this, appropriate controls and improved application techniques will continually be sought. Additional research will be conducted to better understand the pathways by which pesticides leave the site of application and to determine their fate and distribution within the environment.

Methoxychlor [2,2-bis(p-methoxyphenyl)-1,1,1-trichlorethane] is one of the widely used organochlorine insecticides in the United States. The quantity of methoxychlor used by farmers, primarily in application to alfalfa (Medicago Sativa), increased from 317 to 635 metric tons between 1971 and 1976[4]. Methoxychlor was selected as the experimental test compound because of low toxicity to humans and low solubility in water (0.1 mg/l, which is representative of a large class of pesticides). There is

also extensive information available on its sorption to sediments[5], its chemical and photochemical behavior[6,7,8] its microbial degradation[9,10] and its carcinogenicity[11].

In 1973 the registration for use of DDT (dichloro diphenyl trichloroethane) in agriculture was cancelled and methoxychlor was adopted as a replacement compound. It is used for control of a wide range of insect pests on row crops, fruit and shade trees, vegetables, dairy and beef cattle, home gardens and around farm buildings[12]. Although methoxychlor is registered for use on soybeans [Glycine Max (L.) Merrill], its use is relatively limited. A survey of the literature failed to produce any field studies that examined the disappearance (washoff and dryfall) of methoxychlor from soybean foliage under natural rainfall conditions. Most of the earlier studies on washoff of pesticides from leaf surfaces have not been useful for model development[13]. Several mathematical models or assessment tools are currently available that are effective in predicting runoff and/or loadings of agricultural chemicals to water bodies once they are applied to the soil, e.g., the Agricultural Runoff and Management (ARM) model[14,15] and Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS)[16] model. The CREAMS model contains algorithms or equations for describing foliar washoff, but it has not been fully tested. The ARM model does not have this capability in its present form. Beyerlein and Donigian, however, developed an equation describing this process when using the ARM model and indicated a limited data base exists to

confirm the predictive equation[17]. Refined submodels have not been developed because the relationships of pesticide properties to washoff rates as a function of rainfall volume/intensity with time after application and crop type are virtually unknown. The lack of understanding of these relationships limits the utility of predictive tools to assess the behavior of foliar-applied compounds.

The objectives of this study were to provide information that could be used by the EPA in defining research:

- to identify important variables in the interception, persistence and removal (washoff or dryfall) of foliar-applied pesticides; and
- to formulate concepts needed for modeling the behavior of these pesticides.

Such research would provide the ARM model, and other similar loading models, with the capability to handle foliar washoff.

MATERIALS AND METHODS

A field experiment was initiated in 1977 and completed in 1978 near EPA's Environmental Research Laboratory, Athens, Georgia. Each of three experimental test plots consisted of three rows of soybeans (Var. Bragg) 18.3 m long and 0.9 m apart. Three additional rows of soybeans were established outside the field plot area to reduce potential wind and temperature (border) effects. Dates of planting were June 17, 1977, and May 23, 1978. The plots were kept weed free in both years by hand hoeing and soil fertility was maintained for satisfactory crop growth.

In 1977 and 1978, after the soybean plants were in bloom and full canopy cover had developed, methoxychlor wettable powder (Marlate 50W®, E.I. du Pont de Nemours and Co.) was applied at a rate of 4.48 kg/ha active ingredient. Also in 1977, 12 days after application, methoxychlor was reapplied to plot 1 at an active ingredient rate of 6.72 kg/ha and to plot 2 at a rate of 4.48 kg/ha. Reapplication is a common practice in the use of insecticides and the higher application rate for plot 1 was selected to evaluate the impact of a different rate on the washoff potential. Methoxychlor was not reapplied after the initial application in 1978. Methoxychlor was applied using a precalibrated, conventional, CO_2-powered, tri-wheeled applicator similar to the one described by Bailey et al.[18] The height of the applicator spray nozzle was adjusted above the plant canopy to assure uniform pesticide coverage. Applicator nozzle samples were taken to measure delivery volume and concentration of chemical.

In 1978 plots 2 and 3 (hereafter called plot 2) were combined for sampling due to limitations placed upon analytical support. That year an attempt was made to determine the amount of methoxychlor that passed through the plant canopy (through-fall) to the ground on application day. Thirty-two Whatman No. 42 (18.5 cm diameter) filter discs were randomly placed under the canopy of plot 2, and 16 discs were placed under canopy of plot 1. The discs were removed to the laboratory immediately after application and extracted for

methoxychlor. Previous work on the monitoring of herbicide application rates has shown that the filter disc technique provides a good measure of the initial amount applied to soil[2].

Continuous rainfall records and daily air temperature measurements were taken during the study period.

Field Sampling Procedure

Twenty-five whole soybean plants were taken at random from each of the three test plots in 1977 and from one plot (#2) in 1978. The first sample was taken after the plants were relatively dry from the application; frequency of sampling thereafter is shown in Figs. 1 and 2 for 1977 and Fig. 3 for 1978. Statistical tests resulting from the analysis of methoxychlor residue on individual plants prior to starting the study showed that 25 plant samples would provide an estimated error of 22% about the mean at the 5% confidence level. In any event, a larger quantity of plant samples would not have been feasible for sample processing. Samples were taken in late morning after dew had evaporated.

In 1978 teflon-coated pans were placed underneath the canopy of plots 1 and 2 after application in an effort to intercept washoff and dislodgeable residues (dryfall). Three pans (27.9 cm x 43.2 cm) were placed in plot 1, and five pans (20.3 cm x 30.5 cm) were placed in plot 2. Each pan area was identified (wooden stakes) for re-locating to eliminate any possible data discrepancy that might occur if pans were located beneath plants with unknown previous washoff history. By carefully sliding

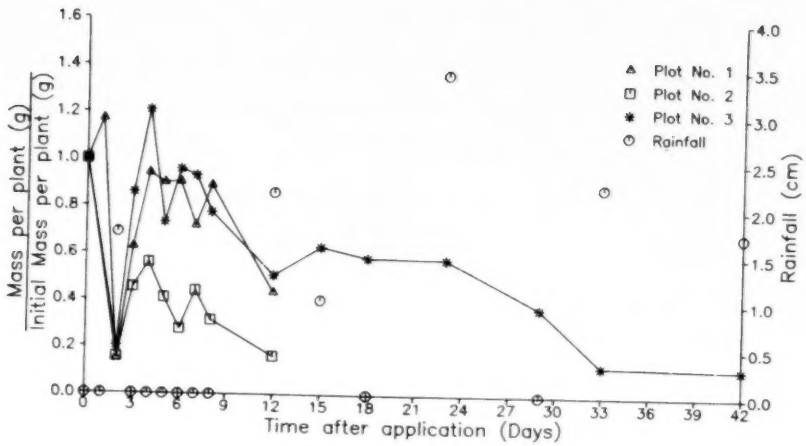

FIGURE 1
Methoxychlor persistence on soybean foliage--initial application 1977

pans beneath the canopy, plot 1 was monitored without workers entering the test area. Pans were removed for residue measurement daily for six days, every other day during the second week and once during the third week after application. Washoff and dryfall from the total plant canopy was calculated by taking the mass per unit area of pans and multiplying by the plot area.

Laboratory Procedure

In 1977 plants were hand chopped, mixed, and the total composite weighed. Two 50-g subsamples were taken for methoxychlor analysis and a 10-g subsample was used for the determination of moisture content. All results were calculated on a dry plant weight basis.

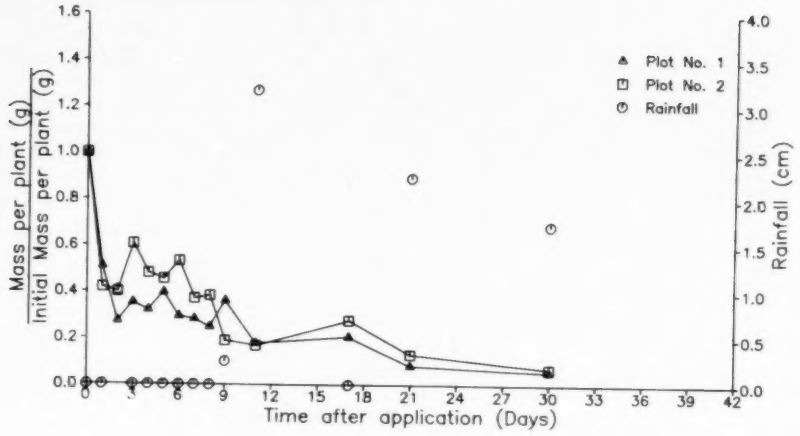

FIGURE 2
Methoxychlor persistence on soybean foliage--reapplication 1977

In 1978 a Hobart 8181D food chopper was available for processing the plants. The mechanical chopper reduced sample preparation time and provided a more homogeneous composite.

Methoxychlor extraction and cleanup for plant samples was conducted using the U.S. Food and Drug Administration method for pesticide residues in non-fatty foods[19]. Method recoveries were 75 ± 5% for samples fortified with methoxychlor formulation (MARLATE 50W) and 77 ± 4% for samples fortified with technical grade methoxychlor. All final sample extracts for methoxychlor were analyzed by GLC using a Tracor MT-220 gas chromatograph equipped with a Coulson electrolytic conductivity detector in the chloride mode. The 0.76-m and 1.83-m glass columns (0.64-cm

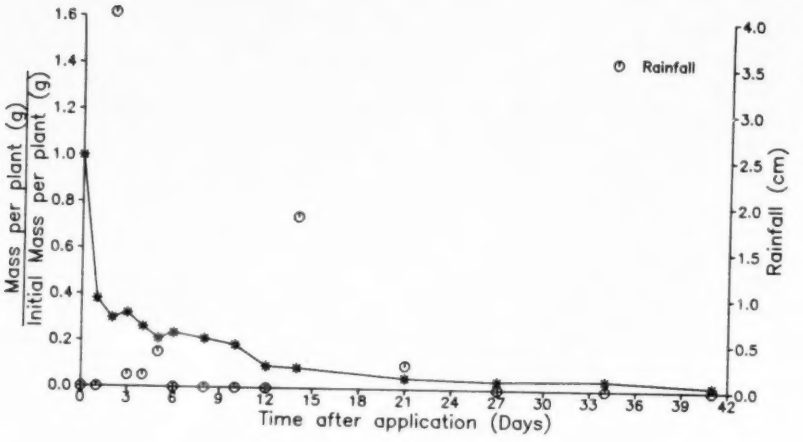

FIGURE 3
Methoxychlor persistence on soybean foliage--1978

O.D.) were packed with 10% DC-200 on 80-100 mesh Gas Chrom Q. Sensitivity for the 0.76-m column was 90 ng (50% Full Scale Deflection [FSD]) at a retention time of 8 minutes. The 1.83-m column was used to check random samples for possible co-extractives that would have interferred with the methoxychlor determination on the shorter column. Sensitivity for the 1.83-m column was 250 ng (50% FSD) at a retention time of 26 minutes. Operating temperatures were: injection, 230^{o}C; furnace, 860^{o}C; transfer block, 240^{o}C; column, 200^{o}C. Gas flow rates were: He, 100 ml/minute; and H_2, 50 ml/minute. The lower limit of detection for methoxychlor using a 25-g sample was 0.1 mg/kg (100 ppb).

Filter discs were extracted with methylene chloride for four hours on a Soxhlet continuous extraction apparatus. The extract was concentrated to a volume of 5-7 ml and transferred to conical test tubes.

Pans containing dryfall only were extracted by rinsing three times with methylene chloride. The rinsings were filtered through glass wool, concentrated to a volume of 5-7 ml and transferred to conical test tubes.

If the pans contained washoff, the water volume was measured, and the sample filtered through glass wool into a separatory funnel. Distilled water was added if necessary to adjust the volume to 1 liter. The pans were rinsed with 100 ml of methylene chloride and the rinse solution was added to the separatory funnel. The methoxychlor was extracted by shaking the funnel vigorously for 2 minutes, allowing the layers to separate, and draining the methylene chloride into a beaker. This entire procedure was repeated two more times using 100 ml and 50 ml rinsing volumes. The combined extracts were concentrated to a volume of 5-7 ml and transferred to conical test tubes.

The remaining solvent in the conical tubes was removed with dry air and the residue was brought to volume with hexane for gas chromatographic analysis.

RESULTS AND DISCUSSION

The distribution between the amount of insecticide reaching the soil (through-fall) versus the amount intercepted by the

TABLE 1
Comparison of Two Sample Processing Techniques: Hand Versus Mechanical Plant Chopping

Days after Application	Methoxychlor Recovered (mg)			
	1977 Hand Chopping Method--duplicate observations			1978 Mechanical Chopping Method--duplicate observations
	Plot-1	Plot-2	Plot-3	Plot 2
3	9.55-7.37	8.69-6.35	3.22-3.81	6.34-6.31
8	4.23-7.73	5.24-4.34	2.93-2.89	4.19-3.29
21	2.96-1.04	2.10-1.16	2.77-1.59	0.95-1.04
34	2.02-0.78	1.17-0.61	0.49-0.49	0.86-0.74
	S^2 (within-sample) = 1.31			S^2 (within-sample) = 0.104

plant canopy must be known to model the behavior of a foliar applied compound. Therefore, an attempt was made to determine the amount of methoxychlor that passes through the plant canopy during application. The resulting through-fall data were very limited and caution must be exercised in their use. The preliminary data, however, shows that more than 19% of the

methoxychlor was deposited on the soil during application. It is evident that additional work is needed for monitoring through-fall.

The 1977 plant samples were chopped by hand because the mechanical chopper was not available until 1978. Therefore, to test for homogeneity of within-sample variances (sample being 25 plants composited and duplicates being subsamples), the within-sample variances for the two methods were estimated independently (Table 1). The statistical model for the 1977 data accounts for variation due to the blocking factor (days), the three replications (plots 1, 2, 3) and an interaction component, the within-sample variance being estimated by the residual mean square. The R^2 value was 0.91, based on 24 observations for the experiment. The estimated within-sample variance is 1.31. The 1978 data consist of one replication with an estimated within-sample variance of 0.104. The R^2 value was 0.99 based on eight observations. An F test (ratio of the two variance estimates) was applied to test the null hypothesis of equal within-sample variances for the two years versus the alternative that the 1977 variance exceeded the 1978 value. The observed F-value (1.31/0.104 = 12.56) is significant at the 0.05 level. The probability of obtaining a more extreme F-value by chance (i.e., under the null hypothesis) is 0.0129. These results as indicated in Table 1, show that within-sample variation for year 1978 is significantly smaller than the within-sample variation for year 1977. Therefore, the mechanical chopper as expected provides a better, more homogeneous sample.

TABLE 2
Methoxychlor Dryfall from Through-Fall Collection Pans--1978

Days After Application	Plot-1+ (mg)	Plot-2++ (mg)
1	66	92
6	23	23
7	3	42
9	2	19
11	1	12
15	2	8

\+ Undisturbed.

++ Workers entered plot.

During 1978, no plant samples were taken from plot 1 and workers removed and replaced through-fall pans without entering the plot. Workers entered plot 2 to collect plant samples and to remove and replace through-fall pans. The losses as shown in Table 2, although small, indicate that some of the material is dislodged by the worker. To test whether plot 1 and plot 2 results were statistically different, a Friedman two-way analysis of variance was applied. The amount of dryfall is shown to be significantly greater in the plot entered by workers (plot 2) than in the undisturbed plot (plot 1). Dryfall or dislodgeable residue, however, accounted for less than 1% of the total material removed from the plants.

TABLE 3
Methoxychlor Washoff, from Through-Fall Collection Pans--1978

Days After Application	Rainfall Volume (cm)	% Loss by Washoff	% Loss/cm Rain
2	4.04	30.48	7.5
3	0.13	0.87	6.7
4	0.13	0.32	2.5
5	0.38	5.45	14.3
13	1.85	16.32	8.8
21	0.25	1.55	6.2

Methoxychlor persistence values on the soybean foliage in the field plots had a mean half-life for the two-year study of 4.4 $\pm$ 1.1 days. This is in agreement with the half-life data (4.9 $\pm$ 2.7 days) presented by Willis et al.[1] for methoxychlor wettable powder. Individual graphs of the ratio of the average mass/plant to the initial average mass/plant were plotted against time after application for each experimental test plot as shown in Figures 1, 2, and 3. During 1977, more variability appears in the first 12 days after application. The apparent loss on the second day after application (Fig. 1) could be due to washoff; however, this could be an artifact developed from the hand chopping method, particularly because the disappearance curve stabilizes for a slower rate of exponential decay.

The 1978 measured washoff data (Table 3) also shows a higher loss occurring on the second day after application. This rainfall event, however, accounted for 30.5% of the total

seasonal washoff loss, which was 33.5% of the initial amount applied. An average of 8 ± 4% of the amount on the plants (prior to rainfall) was lost by washoff, however, for each centimeter of rainfall. These losses are somewhat higher than the findings of Willis et al. (1979)[13] for toxaphene (chlorinated camphene) washoff from cotton (Gossypium hirsutum L.) plants. The difference observed between these two findings could be influenced by the crop type, pesticide characteristics, and formulation, i.e., emulsifiable concentrate vs. wettable powder. Less variability is shown in the 1978 data, (Fig. 3) indicating an improved sample processing technique with the mechanical chopper.

This preliminary investigation clearly shows the need to conduct further research on the behavior of foliar applied compounds under various rainfall volumes and intensities (controlled conditions). Attention should be given to the first two days after application because rapid decay and washoff potential is greatest during this time. The limited scope of this study permitted only the investigation of the parent compound but degradation products, as potential environmental pollutants, should be considered in research efforts to develop an algorithm to fully describe the behavior of foliar-applied pesticides.

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